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ANALYTICAL STUDY OF A SOLAR DEGRADATION MODEL FOR THERMAL CONTROL MATERIALS AND SOME RAMIFICATIONS FOR ACCELERATED SOLAR RADIATION TESTING

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NOTICES

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FOREWORD

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ABSTRACT

A photoreaction-diffusion model for the solar degradation of thermal control materials is mathematically formulated and analyzed. The governing differential equation for the concentration of defect specie created in the material by radiation is derived, and an analytical solution is obtained for appropriate boundary conditions. From this solution for the concentration N_i of the ith-type defects, an analytical expression is derived for the number Q_i of the ith-type defects present in a material layer of depth x and unit irradiated area. These analytical relations are used to predict the radiation-induced increase in the absorption coefficient and absorption optical thickness of a hypothetical thermal control material exposed to damaging ultraviolet irradiance equal to that of the sun. The solutions for N_i and Q_i are also used to better define the environmental parameters which must be controlled during solar radiation testing of thermal control coatings. For example, the time-irradiance reciprocity principle often employed in accelerated solar testing is investigated by use of the aforementioned solutions and is found to be invalid for materials which degrade according to the photoreaction-diffusion model.

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APPENDIX

Illustrations

NOMENCLATURE

D	Diffusion coefficient
erfc	Complementary error function
F_{-1}	Function defined in Eq. (8)
G_{-1}	Function defined in Eq. (13)
I	Radiant energy flux in photons/sec-cm^2
k	Quantum yield, net number of defects created per absorbed photon
N	Defect concentration
n	Number of different types of defect specie
P	Pressure
Q	Number of given type of defects present in a layer of depth x and unit irradiated area
R	Reflectance
T	Temperature
t	Irradiation time
x	Local depth in material (see Fig. 1)
α	Absorptance
γ	Wavelength of damaging radiation
Δ	Change in an associated quantity
ϵ	Absorption coefficient
λ	Wavelength of radiation
σ_a	Absorption cross section
τ	Absorption optical thickness

SUBSCRIPTS

i	ith-type defect specie
o	Conditions at surface
r	Reference value

s   Solar value

x   Conditions at depth x

γ Value at wavelength γ

$,\gamma$ $\dfrac{d}{d\gamma}$

λ Value at wavelength λ

SECTION I
INTRODUCTION

In several previous studies of solar ultraviolet radiation effects on the zinc oxide (ZnO) pigments of thermal control coatings (Refs. 1 through 3), the investigators postulated that a photoreaction-diffusion damage mechanism causes the changes induced in the optical properties of the zinc oxide. They also suggested that the same type of mechanism causes the ultraviolet (UV)-induced damage observed for similar thermal control materials such as titanium dioxide (TiO_2) and tin oxide (SnO_2). In the work presented here, a photoreaction-diffusion model for the solar degradation of thermal control materials of this type is mathematically formulated and analyzed. That was the main objective of this study. There were several secondary objectives. One was to deduce a mathematical model which, when completely formulated, might permit the theoretical prediction of solar absorptance change of spacecraft thermal control surfaces as a function of irradiation time, irradiance level, and surface temperature. An example application of this model is given and used to predict the induced absorption coefficient and the increase in absorption optical thickness (Ref. 4) of a hypothetical thermal control material exposed to damaging UV irradiance equal to that of the sun. Another objective was to mathematically define the space environment conditions which should be simulated in laboratory tests of solar degradation effects on thermal control coatings. Among the environmental effects considered are the magnitude and spectral distribution of the damaging irradiance. For example, a theoretical investigation was made of the time-irradiance reciprocity principle used in accelerated solar radiation testing.

SECTION II
FORMULATION OF MATHEMATICAL MODEL FOR PHOTOREACTION-DIFFUSION DAMAGE MECHANISM

2.1 PHYSICAL MODEL OF DAMAGE MECHANISM

The photoreaction-diffusion damage mechanism postulated for the solar degradation of thermal control materials basically assumes that ultraviolet photons absorbed near the surface of the material possess sufficient energy to produce defects by photochemical reaction. The defects are created within the penetration depth of the damaging irradiation and then diffuse into the material bulk as the generation process continues at a decreasing rate near the surface. These defects will

absorb radiation in a spectrally dependent manner and hence may cause a significant increase in the parent material absorption properties at wavelengths in the visible and infrared. It is assumed that the change in monochromatic absorptance at these wavelengths is a function of the defect concentration in the parent material.

2.2 MATHEMATICAL MODEL AND DERIVATION OF GOVERNING EQUATIONS

A mathematical model for the UV degradation of thermal control materials may be formulated in the following manner. The material is assumed to be in a low pressure vacuum environment. Its surface, as shown in Fig. 1 (Appendix), is exposed to damaging irradiation of wavelengths lying within the differential wavelength interval $d\gamma$. The spectral irradiance at wavelength γ lying within $d\gamma$ is denoted by $I_{0,\gamma}$ and the total irradiance with $d\gamma$ is given by $I_{0,\gamma}d\gamma$. Most of this incident radiant energy flux will be absorbed by the material within a depth of less than 0.1 micron from the surface and there generate by photoreaction $k_{i\gamma}$ ith-type defects per absorbed photon. Figure 1 shows a cross section of this region of the material with a differential element dx located at a distance x from the surface $(x = 0)$. The concentration of the ith defect specie produced by damaging irradiation of wavelength γ and now present in dx at time t is denoted by $N_{i,\gamma}d\gamma$. Hence, the symbol $N_{i,\gamma}$ can be interpreted as the concentration of the ith-type defects created per wavelength interval $d\gamma$ by damaging radiation of wavelength γ. The net radiant energy flux downward at depth x is shown in Fig. 1 and denoted by $I_{x,\gamma}d\gamma$. Figure 1 also shows the diffusion fluxes $-D_i \dfrac{\partial N_{i,\gamma}}{\partial x} d\gamma$ which exist in the material because of the presence of specie i. The symbol D_i denotes the diffusion coefficient of the ith defect specie in the parent material. It is assumed that there are no interactions between defects.

To derive the governing differential equations for the defect species concentrations, the law of mass conservation is assumed for the ith defect specie present in the differential element dx shown in Fig. 1. This yields the following partial differential equation

$$\frac{\partial N_{i,\gamma}}{\partial t} = -k_{iy} \frac{\partial I_{x,\gamma}}{\partial x} + \frac{\partial}{\partial x}\left(D_i \frac{\partial N_{i,\gamma}}{\partial x}\right) \tag{1}$$

where $k_{i\gamma}$ is designated as the ith defect quantum yield (Ref. 5) of the material for damaging radiation of wavelength γ. From this equation it can be seen that an analytical expression for $I_{x,\gamma}$ is needed. For a

collimated radiant flux incident normally on the surface as shown in Fig. 1,* the analytical relation for $I_{x, \gamma}$, assuming internal scattering to be negligible at wavelength γ, is

$$I_{x,\gamma} = (1 - R_\gamma) I_{o,\gamma} \exp{(- \epsilon_\gamma x)} \qquad (2)$$

Hence,

$$\frac{\partial I_{x,\gamma}}{\partial x} = -(1 - R_\gamma) \, \epsilon_\gamma \, I_{o,\gamma} \exp{(-\epsilon_\gamma x)} \qquad (3)$$

where R_γ and ϵ_γ are, respectively, the reflectance and linear absorption coefficient for the parent material at the wavelength of the damaging radiation. Thus, from Eq. (1) with D_i independent of x and Eq. (3), the governing differential equation for the concentration of defect specie i is

$$\frac{\partial N_{i,\gamma}}{\partial t} = k_{i\gamma}(1 - R_\gamma) \, \epsilon_\gamma \, I_{o,\gamma} \exp{(-\epsilon_\gamma x)} + D_i \, \frac{\partial^2 N_{i,\gamma}}{\partial x^2} \qquad (4)$$

If n different types of noninteracting defect specie are generated by damaging radiation of wavelength γ, there will be n different equations of the form of Eq. (4).

2.3 FACTORS POTENTIALLY INFLUENCING PHYSICAL PARAMETERS $I_{o, \gamma}$, D_i, ϵ_γ, R_γ, AND $k_{i\gamma}$

As noted by the subscript γ, the physical parameters $I_{o, \gamma}$, ϵ_γ, R_γ, and $k_{i\gamma}$ appearing in Eq. (4) can all be a function of the wavelength of the damaging radiation. These parameters along with D_i may also be a function of other factors. For example, the spectral irradiance $I_{o, \gamma}$ might be a function of time, t. Potentially influencing factors for the other parameters are described below.

First, consider D_i, the diffusion coefficient of the ith defect specie. In general, D_i can depend on the temperature of the parent material, the concentration of the ith-type specie, and also the concentrations of any other types of specie which may be present. However, the dependence of D_i on concentration is usually negligible except at very high concentration levels (Ref. 6).

Next, consider the absorption coefficient and reflectance of the parent material at the wavelength of the damaging radiation, ϵ_γ and R_γ, respectively. In general, it is felt that ϵ_γ will not vary greatly with

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*In Fig. 1, it is assumed that the penetration depth of the damaging irradiation is much less than the material thickness.

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location in the thermal control material and hence can be considered a constant with respect to x. This assumption is employed throughout the analysis. In addition, it is assumed that ϵ_γ is not a function of time, t. This assumption physically means that although defects generated by damaging irradiation of wavelength γ can absorb radiation at that same wavelength, the resulting increase in absorption at γ is negligible relative to the initial absorption at γ. An illustrative problem presented later in the text will prove that this assumption is definitely valid. As for R_γ, the reflectance of the material at the wavelength of the damaging radiation, it also is assumed constant with respect to time, t.

Finally, it is necessary to consider $k_{i\gamma}$, the ith defect quantum yield. As noted earlier, $k_{i\gamma}$ is a function of the wavelength of the damaging radiation (Ref. 5). It also can be a function of the radiant exposure of the surface. For thermal control materials of the type mentioned previously, $k_{i\gamma}$ is likely to decrease rapidly as the radiant exposure of the surface increases (Ref. 7). It is speculated that $k_{i\gamma}$ is also a function of the irradiance level of the damaging radiation (Ref. 8). In addition, the temperature of the material can affect $k_{i\gamma}$ through its influence on secondary chemical processes taking place in the medium (Ref. 8). It is also possible that the pressure of the vacuum environment in which the material is located could affect $k_{i\gamma}$. This would happen if the pressure were not maintained at a low enough level to ensure that the concentration of any gases present was insufficient to influence the secondary chemical processes occurring in the material and on its surface (Ref. 7).

SECTION III
AN ANALYTICAL EXPRESSION FOR THE CONCENTRATION OF
ith-TYPE DEFECT SPECIE

An analytical solution has been derived to Eq. (4) for $I_{0,\gamma}$ constant with time and D_i independent of concentration. This solution was obtained under the following assumptions: (1) Initially there are no radiation-induced defects present in the material, (2) once the irradiation begins, none of the defects created by it will be lost through the irradiated surface (x = 0), and (3) none of the radiation-induced defects will penetrate to the material boundary opposite the irradiated surface. Mathematically, these assumptions may be expressed as the following initial and boundary conditions on Eq. (4):

$$t = 0, N_{i,\gamma} = 0 \text{ for } x \geq 0$$

$$t > 0, \begin{cases} \dfrac{\partial N_{i,\gamma}}{\partial x}\bigg|_{x=0} = 0 \\ N_{i,\gamma} \to 0 \text{ as } x \to \infty \end{cases} \tag{5}$$

The solution to Eq. (4), subject to the conditions stated in Eq. (5), has been obtained by operational techniques for $k_{i\gamma}$ being the following function* of radiant exposure,

$$k_{i\gamma} = k_{i\gamma r} \left(\frac{I_{o,\gamma} t}{I_{r,\gamma} t_r}\right)^{-\frac{1}{2}} \tag{6}$$

This solution to Eqs. (4), (5), and (6) takes the form

$$N_{i,\gamma} = \left(\frac{m_r}{D_i}\right)^{\frac{1}{2}} (1 - R_\nu) \, k_{i\gamma r}(I_{r,\gamma} I_{o,\gamma})^{\frac{1}{2}} \, F_{-1}\left[2\epsilon_\gamma (D_i t)^{\frac{1}{2}}, \frac{x}{2(D_i t)^{\frac{1}{2}}}\right] \tag{7}$$

where, noting $\epsilon_\gamma x = 2\epsilon_\gamma (D_i t)^{\frac{1}{2}} \cdot \dfrac{x}{2(D_i t)^{\frac{1}{2}}}$

$$F_{-1}\left[2\epsilon_\gamma (D_i t)^{\frac{1}{2}}, \frac{x}{2(D_i t)^{\frac{1}{2}}}\right] = \mathrm{erfc}\left[\frac{x}{2(D_i t)^{\frac{1}{2}}}\right] \tag{8}$$

$$-\exp(\epsilon_\gamma^2 D_i t - \epsilon_\gamma x) \cdot \mathrm{erfc}\left[\epsilon_\gamma (D_i t)^{\frac{1}{2}}\right]$$

$$+ \frac{1}{2} \cdot \exp(\epsilon_\gamma^2 D_i t - \epsilon_\gamma x) \cdot \mathrm{erfc}\left[\epsilon_\gamma (D_i t)^{\frac{1}{2}} - \frac{x}{2(D_i t)^{\frac{1}{2}}}\right]$$

$$- \frac{1}{2} \cdot \exp(\epsilon_\gamma^2 D_i t + \epsilon_\gamma x) \cdot \mathrm{erfc}\left[\epsilon_\gamma (D_i t)^{\frac{1}{2}} + \frac{x}{2(D_i t)^{\frac{1}{2}}}\right]$$

Figure 2 presents this solution for $N_{i,\gamma}$ in the dimensionless form F_{-1} with $\dfrac{x}{2(D_i t)^{1/2}}$ taken as the independent variable and $2\epsilon_\gamma(D_i t)^{1/2}$ as a parameter. Note that F_{-1} is essentially the same for all values of $2\epsilon_\gamma(D_i t)^{1/2} \geq 10$.

An analysis of Eq. (7) indicates that it can be used to predict analytically the x-distribution of $N_{i,\gamma}$ as a function of time, t, and the spectral irradiance, $I_{o,\gamma}$. Thus, $N_{i,\gamma} d\gamma$, the concentration of the ith defect specie generated by damaging radiation lying within the small wavelength interval $d\gamma$, can be predicted as a function of the same variables. For the case

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*The subscript r on the symbols in Eq. (6) denotes reference values of the associated physical quantities.

where the material is irradiated with total radiation, the concentration of the ith defect specie, N_i, must be obtained by integrating $N_{i, \gamma}$ of Eq. (7) over all damaging wavelengths since photons at other wavelengths besides γ may also produce defect specie of type i. The resulting expression for N_i is

$$N_i = \left(\frac{\pi t_r}{D_i}\right)^{\!\!\mathscr{V}} \int_0^{\gamma_i(T)} (1 - R_\gamma)\, k_{i\gamma r}\, (I_{r,\gamma}\, I_{0,\gamma})^{\!\mathscr{V}}\, F_{-1}\!\left[2\epsilon_\gamma (D_i t)^{\mathscr{V}},\ \frac{x}{2\,(D_i t)^{\mathscr{V}}}\right] d\gamma \qquad (9)$$

where γ_i is the largest wavelength at which incident photons will produce defect specie of type i. It is indicated that γ_i can be a function of the material temperature, T. This is because the wavelength at which the material absorption edge occurs may shift with temperature (Ref. 3). Note that the concentration of defects at the surface can be obtained directly from Eq. (9) and is

$$N_{io} = \left(\frac{\pi t_r}{D_i}\right)^{\!\!\mathscr{V}} \int_0^{\gamma_i} (1 - R_\gamma)\, k_{i\gamma r}(I_{r,\gamma}\, I_{0,\gamma})^{\!\mathscr{V}}\, F_{-1}\,[2\epsilon_\gamma\,(D_i t)^{\mathscr{V}},\ 0]\, d\gamma$$

$$\qquad (10)$$

$$F_{-1}\,[2\epsilon_\gamma\,(D_i t)^{\mathscr{V}}, 0] = 1 - \exp\,(\epsilon_\gamma^2\, D_i t)\ \mathrm{erfc}\,[\epsilon_\gamma\,(D_i t)^{\mathscr{V}}]$$

An analysis of Eq. (9) indicates that it can be used to predict the concentration distribution of ith-type defects created in the irradiated material by radiation of wavelengths lying within the wavelength interval $(0, \gamma_i)$. This can be done as a function of irradiation time and the magnitude and spectral distribution of the damaging irradiance. Such an expression is useful because the concentration N_i determines the increase in the spectral absorption coefficient of the material caused by the presence of ith-type defect specie.

SECTION IV
NUMBER OF ith-TYPE DEFECTS PRESENT IN A LAYER OF DEPTH x AND UNIT IRRADIATED AREA

The number Q_i of ith-type defects present in a layer of depth x and unit irradiated area is mathematically related to the specie concentration N_i by the expression

$$Q_i = \int_0^x N_i\, dx' \qquad (11)$$

Thus, Q_i is the integral of the specie concentration over depth x into the material. This integral has been evaluated for N_i given by Eq. (9) and the resulting expression is

$$Q_i = \left(\frac{\pi r_r}{D_i}\right)^{1/2} \int_0^{y_i(T)} \frac{(1 - R_\gamma)\, k_{i\gamma r}\, (I_{r,\gamma}\, I_{o,\gamma})^{1/2}\, G_{-1}\left[2\epsilon_\gamma\,(D_i t)^{1/2},\, \frac{x}{2(D_i t)^{1/2}}\right]}{\epsilon_\gamma}\, dy \qquad (12)$$

where

$$G_{-1}\left[2\epsilon_\gamma (D_i t)^{1/2},\, \frac{x}{2(D_i t)^{1/2}}\right] = \exp\left(\epsilon_\gamma^2\, D_i t - \epsilon_\gamma x\right) \cdot \operatorname{erfc}\left[\epsilon_\gamma (D_i t)^{1/2}\right]$$

$$+ 2\epsilon_\gamma (D_i t/\pi)^{1/2}\left(1 - \exp\left(\frac{-x^2}{4\,D_i t}\right)\right) + \epsilon_\gamma x\, \operatorname{erfc}\left[\frac{x}{2\,(D_i t)^{1/2}}\right]$$

$$- \frac{1}{2} \cdot \exp\left(\epsilon_\gamma^2\, D_i t - \epsilon_\gamma x\right) \cdot \operatorname{erfc}\left[\epsilon_\gamma (D_i t)^{1/2} - \frac{x}{2(D_i t)^{1/2}}\right]$$

$$- \frac{1}{2} \cdot \exp\left(\epsilon_\gamma^2\, D_i t + \epsilon_\gamma x\right) \cdot \operatorname{erfc}\left[\epsilon_\gamma (D_i t)^{1/2} + \frac{x}{2(D_i t)^{1/2}}\right] \qquad (13)$$

The function G_{-1} is displayed in Fig. 3 with $\dfrac{x}{2(D_i t)^{1/2}}$ as the independent variable and $2\epsilon_\gamma(D_i t)^{1/2}$ taken as a parameter. Note that G_{-1} can also be interpreted as

$$Q_{i,\gamma} \Big/ \frac{(\pi r_r/D_i)^{1/2}\, (1 - R_\gamma)\, k_{i\gamma r}\, (I_{r,\gamma}\, I_{o,\gamma})^{1/2}}{\epsilon_\gamma} \qquad (14)$$

$$Q_{i,\gamma} \equiv \int_0^x N_{i,\gamma}\, dx'$$

Equation (12) for Q_i can be used to predict the number of ith defects present in a material layer of depth x and unit irradiated area as a function of irradiation time and the magnitude and spectral distribution of the damaging irradiance. Such an expression is particularly useful since Q_i strongly influences the increase in absorption optical thickness resulting from the presence of ith-type defects. This increase in absorption optical thickness is one of the most important parameters governing the induced spectral absorptance of thermal control materials.

SECTION V
RELATION OF N_i AND Q_i TO THEORETICAL PREDICTIONS
OF SOLAR ABSORPTANCE CHANGE

5.1 GENERAL DISCUSSION OF MATHEMATICAL MODEL

In a mathematical model for predicting the solar absorptance change of spacecraft thermal control surfaces as a function of irradiation time and irradiance level, it is assumed that defects are generated in thermal control materials by absorption of high energy photons. If the defect concentration, N_i, and the number, Q_i, of ith-type defects per unit irradiated area could be predicted, then knowledge of the basic absorption properties of the defect would allow predictions of the increase in the material spectral absorption coefficient and absorption optical thickness. With the increases in absorption coefficient and absorption optical thickness determined, one would then solve the radiative transport equation with these variables present. The resulting solutions for the intensity and radiant flux could be used to predict the change in the material spectral absorptance as a function of irradiation time and irradiance level.

Obtaining analytical relations between the irradiation time and N_i and Q_i would be an important step in any model used for theoretically predicting the change in solar absorptance of thermal control materials. Another important step would be to develop an analytical relation between N_i, Q_i and the spectral absorptance increase of these materials.

5.2 ASSUMED RELATIONS BETWEEN N_i, Q_i AND THE INDUCED ABSORPTION
PROPERTIES OF THERMAL CONTROL MATERIALS

Any attempt to develop analytical relations between N_i, Q_i and the increase in spectral absorptance of thermal control materials will first require that theoretical expressions be established between the induced absorption properties of the material and N_i and Q_i. This study assumes that a linear relation exists between the induced absorption coefficient and the defect specie concentration. Thus, the increase in the monochromatic absorption coefficient of the parent material caused by the presence of ith-type defect specie, $\Delta\epsilon_{\lambda i}$, is the product of N_i and the absorption cross section for the ith defect specie at wavelength λ, $\sigma_{ai\lambda}$.

$$\Delta\epsilon_{\lambda i} = \sigma_{ai\lambda} N_i \tag{15}$$

where $\Delta\epsilon_{\lambda i}$ will be referred to, for conciseness, as the induced monochromatic absorption coefficient of the material for type i defect specie.

When n different types of defect specie are present, the total induced absorption coefficient of the material, at wavelength λ, $\Delta\epsilon_\lambda$, is assumed to be the linear sum of the effect of each type of specie, or

$$\Delta\epsilon_\lambda = \sum_{j=1}^{n} \Delta\epsilon_{\lambda i} = \sum_{j=1}^{n} \sigma_{ai\lambda} N_i \qquad (16)$$

This equation and the assumption on which it is based ignore any interaction effects that might occur between different defect species.

Once a relation between $\Delta\epsilon_\lambda$ and N_i is specified, it is possible to establish a connection between the increase in monochromatic absorption optical thickness, $\Delta\tau_\lambda$, and N_i. For conciseness, $\Delta\tau_\lambda$ will be referred to as the induced absorption optical thickness of the material at wavelength λ. An analytical expression between $\Delta\tau_\lambda$ and N_i is obtained from Eq. (16) and the definition of $\Delta\tau_\lambda$,

$$\Delta\tau_\lambda = \int_0^x \Delta\epsilon_\lambda dx = \sum_{j=1}^{n} \sigma_{ai\lambda} \int_0^x N_i dx' = \sum_{j=1}^{n} \sigma_{ai\lambda} Q_i \qquad (17)$$

Equation (17) illustrates the relation between $\Delta\tau_\lambda$ and N_i, or Q_i. This relation, of course, implicitly contains the assumptions on which Eqs. (15) and (16) were based. Note that the induced absorption optical thickness resulting from the presence of an ith-type defect specie, $\Delta\tau_{\lambda i}$, is given by the expression

$$\Delta\tau_{\lambda i} = \int_0^x \Delta\epsilon_{\lambda i} dx' = \sigma_{ai\lambda} \int_0^x N_i dx' = \sigma_{ai\lambda} Q_i \qquad (18)$$

SECTION VI
THEORETICAL PREDICTIONS FOR THE SOLAR-INDUCED ABSORPTION PROPERTIES OF A HYPOTHETICAL THERMAL CONTROL MATERIAL

A simple example will now be given to illustrate the application of the mathematical model just described. Assume a hypothetical material to be exposed to a UV irradiance whose magnitude and spectral distribution is equal to that of the sun at one astronomical unit (Ref. 9). During this exposure the material is located in a high vacuum and maintained at a constant temperature of approximately 300°K. The spectral (ultraviolet and visible) absorption coefficient of this material prior to exposure is assumed to be identical to the one shown in Fig. 4. Note that ϵ_γ, the absorption coefficient in the damaging wavelength interval $(0 \leq \gamma \leq 385$ nm) is taken constant at a value of 3×10^5 cm^{-1}. In turn,

R_γ, the spectral reflectance of the material in this interval, is assumed constant at a value of 0.07.

6.1 CONCENTRATION OF THE ith DEFECT SPECIE, N_i

Equation (9) is used to calculate the concentration distribution of the ith defect specie. This specie is assumed to have a diffusion coefficient in the parent material of $D_i = 1.5 \times 10^{-13}$ cm^2/sec. The reference UV spectral irradiance in Eq. (9), $I_{r,\gamma}$, is taken to be that of the sun, $I_{s,\gamma}$, and the reference irradiation time, t_r, is chosen as one second. For these reference conditions, the spectrally weighted (for solar irradiance $I_{s,\gamma}$) ith defect quantum yield

$$\bar{k}_{is} \equiv \int_0^{\gamma_i} k_{i\gamma r}\, I_{s,\gamma}\, d\gamma \Big/ \int_0^{\gamma_i} I_{s,\gamma}\, d\gamma \qquad (19)$$

is assumed to be 10^{-4} defects per photon. Figure 5 presents the defect concentration distribution in the parent material with irradiation time shown as a parameter. It is seen that adjacent to the surface of the material there is a layer of high and essentially uniform concentration. As a result of diffusion, the width of this layer increases slowly with time. Note that the defect concentration increases rapidly with irradiation time until a limiting value is reached.

Figure 6 presents the time dependence of the defect concentration at various depths in the material. The curve labeled x = 0 is the defect surface concentration, N_{io}, as given by Eq. (10). Note how rapidly the surface concentration increases during the early stages of irradiation. After this large initial increase, the surface concentration is essentially constant with time. Similar behavior is observed for the defect concentration at a depth of 1.0 micron. At a depth of 10 microns, the rate of defect concentration increase is much less during the initial stages of radiation. However, after this initial radiation stage, the rate of concentration increase at 10 microns is greater than that of the depths closer to the surface (x = 0, 1.0μ). Hence, the defect concentration at all three depths will eventually become equal.

6.2 NUMBER OF ith DEFECT SPECIE PER UNIT IRRADIATED AREA

In Fig. 7, the number of ith-type defects, Q_i, present per unit irradiated area from the surface to depth x is displayed as a function of depth into the material with irradiation time as a parameter. This figure shows that for a given irradiation time, Q_i increases sharply

with depth into the material until a certain depth is reached. At this depth, Q_i becomes constant and remains so for greater depths. This constant value of Q_i represents the total number of ith-type defects created in the material per unit irradiated area during the specified irradiation time. The depth at which this constant value of Q_i is achieved increases with irradiation time because of defect diffusion. Note that for a layer of given depth, Q_i increases sharply with irradiation time until some limiting or saturation value is attained.

6.3 INDUCED ABSORPTION COEFFICIENT, $\Delta\epsilon_{\lambda i}$

Figure 8 presents the increase in the absorption coefficient of the parent material at a depth of one micron caused by the presence of ith-type defects. Irradiation time is shown as a parameter, and the absorption coefficient of the material prior to irradiation is also indicated. In computing $\Delta\epsilon_{\lambda i}$, Eqs. (9) and (15) were used. For illustrative purposes, the ith-specie absorption cross section, $\sigma_{ai\lambda}$, was taken as 2×10^{-17} cm^2 and assumed to be independent of wavelength. From Fig. 8, it is seen that the induced absorption coefficient, $\Delta\epsilon_{\lambda i}$, increases rapidly with irradiation time and at approximately 10 hr equals the initial absorption coefficient of the parent material in the visible wavelength range, 2×10^1 cm^{-1}. At about 2000 hr, the induced absorption coefficient reaches a saturation value of approximately 10 times the visible absorption coefficient of the parent material prior to irradiation. However, in the damaging wavelength interval (0, 385 nm), the induced absorption coefficient is less than 1/1000 of the absorption coefficient of the parent material prior to irradiation. Thus, $\Delta\epsilon_{\gamma i}/\epsilon_{\gamma}$ is negligible and the change in the absorption coefficient of the parent material in the damaging wavelength range can be ignored. This, of course, validates the assumption made previously about ϵ_{γ} not varying with irradiation time.

6.4 INDUCED ABSORPTION OPTICAL THICKNESS, $\Delta\tau_{\lambda i}$

Figure 9 displays $\Delta\tau_{\lambda i}$, the increase in absorption optical thickness of the parent material caused by the presence of ith-type defect specie. It is presented as a function of irradiation time, with depth into the material taken as a parameter. Equations (12) and (18) were used in evaluating $\Delta\tau_{\lambda i}$. As shown in Fig. 9, $\Delta\tau_{\lambda i}$ increases very rapidly during the first few hours of irradiation. After this period, $\Delta\tau_{\lambda i}$ continues to increase with irradiation time but at a much slower rate. Most all of the induced absorption optical thickness $\Delta\tau_{\lambda i}$ occurs within

50 microns of the surface. For irradiation times of 2000 hr and greater, this value of $\Delta\tau_{\lambda i}$ is approximately 0.2.

SECTION VII
USE OF THE N_i RELATION TO MATHEMATICALLY DEFINE THE ENVIRONMENTAL PARAMETERS INVOLVED IN SOLAR RADIATION TESTING OF THERMAL CONTROL COATINGS

As mentioned in the introduction, one of the objectives of this study is to mathematically define the space environment conditions which should be simulated in laboratory tests of solar radiation effects on thermal control coatings. Since the solar-induced optical properties $(\Delta\epsilon_\lambda, \Delta\tau_\lambda, \Delta\alpha_\lambda)$* are ultimately a function of

$$N_i \left(Q_i = \int_0^x N_i dx\right)$$

Eq. (9) will be used to accomplish this objective. Thus, with $I_{r,\gamma}$ taken as the UV spectral irradiance of the sun, $I_{s,\gamma}$ and t_r as some reference solar irradiation time, t_s,

$$N_i = \left(\frac{\pi t_s}{D_i(T)}\right)^{\frac{1}{2}} \int_0^{\gamma_i(T)} [1 - R_\gamma] \, k_{i\gamma s} \, (P, T) \, [I_{s,\gamma} I_{o,\gamma}]^{\frac{1}{2}} \, F_{-1} \left[2\epsilon_\gamma (D_i t)^{\frac{1}{2}}, \frac{x}{2(D_i t)^{\frac{1}{2}}}\right] d\gamma \quad (20)$$

where $k_{i\gamma s}$ is the value of $k_{i\gamma r}$ for the condition $I_{r,\gamma} = I_{s,\gamma}$, $t_r = t_s$.

From Eq. (20), it can be seen that $k_{i\gamma s}$, R_γ, and ϵ_γ can all depend on the wavelength of the damaging irradiation and each influences the value of N_i. Thus, in laboratory tests of solar degradation effects on thermal control coatings, the spectral distribution of the irradiance on the surface, $I_{o,\gamma}$, should closely simulate that of the sun for the wavelength range $(0, \gamma_i)$. This means that the resultant spectral distribution of the energy source and the intervening optics (e. g., windows and filters) between it and the test surface should closely approximate that of the sun over the interval $(0, \gamma_i)$.

It is also seen in Eq. (20) that the magnitude of the spectral irradiance $I_{o,\gamma}$ influences the value of N_i. Thus, for solar radiation testing of thermal control coatings, both the magnitude and spectral distribution of the irradiance on the surface should be nearly equal to that of the

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*$\Delta\alpha_\lambda$ is defined as the induced spectral absorptance of the parent material.

sun in the wavelength interval $(0, \gamma_i)$. The ramifications of this conclusion for accelerated solar radiation testing are discussed in the next section.

Equation (20) also shows that N_i can depend on the temperature of the material during irradiation because D_i, $k_{i\gamma s}$, and the wavelength at which the material absorption edge occurs, γ_i, all vary with temperature. Thus, the material temperature should be controlled during a solar radiation test and maintained at a value near that expected in flight.

Finally, it is seen that N_i of Eq. (20) can also be influenced by the pressure of the vacuum environment in which it is located. As was discussed earlier, this is because of the potential dependence of $k_{i\gamma}$ on the concentration level of gases in the surrounding environment. Thus, solar radiation testing of thermal control coatings must be performed in a high vacuum and measurements of $\Delta\epsilon_\lambda$, $\Delta\tau_\lambda$, and $\Delta\alpha_\lambda$ must be made in place.

SECTION VIII
VALIDITY OF THE TIME-IRRADIANCE RECIPROCITY PRINCIPLE USED IN ACCELERATED SOLAR RADIATION TESTING

The discussion in the previous section on solar radiation testing of thermal control coatings indicates that to obtain reliable data for $\Delta\alpha_\lambda$, both the magnitude and spectral distribution of the irradiance on the surface should closely approximate that of the sun in the wavelength interval $(0, \gamma_i)$. This conclusion, of course, questions the reliability of data obtained in accelerated solar radiation testing where, to save time, it is assumed that the same test results for $\Delta\alpha_\lambda$ can be obtained by substituting high-intensity UV source irradiance for irradiation time. The validity of this time-irradiance reciprocity principle is investigated in the following paragraphs by use of the equations developed earlier in the study.

Since the induced spectral absorptance of the parent material caused by the presence of defect specie i, $\Delta\alpha_{\lambda i}$, is a function of the induced absorption coefficient $\Delta\epsilon_{\lambda i} = f(N_i)$ and the induced absorption optical thickness $\Delta\tau_{\lambda i} = f(Q_i)$, Eqs. (15), (9), (18), and (12) will be used to accomplish the aforementioned investigation. It will be assumed that if the reciprocity principle does not hold for $\Delta\epsilon_{\lambda i}(N_i)$ and $\Delta\tau_{\lambda i}(Q_i)$, it will not hold for $\Delta\alpha_{\lambda i}$. The properties of the parent material and the ith defect specie will be taken the same as those used in the previous

illustrative example. Ultraviolet irradiance levels of 1 and 10 "Suns" will be used. The spectral distribution of both irradiances in the wavelength interval $(0, \gamma_i = 385$ nm) is assumed to be that of the sun (Ref. 9). Figure 10 presents the surface (x = 0) value of the induced absorption coefficient $\Delta\epsilon_{\lambda i}$ as a function of radiant exposure in Equivalent Sun Hours (ESH) with UV irradiance level in "Suns" shown as a parameter. For a given radiant exposure, $\Delta\epsilon_{\lambda i}$ is seen to be significantly greater at an irradiance of 10 "Suns" than at 1 "Sun" irradiance. If the time-irradiance reciprocity principle held, there would be no effect of irradiance level on $\Delta\epsilon_{\lambda i}$, and only a single curve equal to the one "Sun" value of $\Delta\epsilon_{\lambda i}$ would appear in Fig. 10.

Figure 11 displays the value of $\Delta\epsilon_{\lambda i}$ at a depth of 1 micron in the material. It is seen that for a radiant exposure less than 60 ESH, $\Delta\epsilon_{\lambda i}$ at 1 "Sun" irradiance is greater than $\Delta\epsilon_{\lambda i}$ at a UV irradiance level of 10 "Suns." However, for a radiant exposure greater than 60 ESH, $\Delta\epsilon_{\lambda i}$ at 10 "Suns" exceeds $\Delta\epsilon_{\lambda i}$ at 1 "Sun", which was the expected result for all values of ESH. This weird behavior of $\Delta\epsilon_{\lambda i}$ with irradiance and radiant exposure in ESH is a result of defect diffusion. It can be explained by noting that for an equivalent number of sun hours of radiant exposure a defect generated by 1 "Sun" irradiance can diffuse into the material 10 times as long as a defect created by an irradiance of 10 "Suns." Thus, for depths in the material which are somewhat greater than the penetration depth of the damaging irradiation, the defect concentration N_i and hence $\Delta\epsilon_{\lambda i}$ will be larger for the lower irradiance level until some particular ESH of radiant exposure is reached.

In Fig. 12, the induced absorption optical thickness $\Delta\tau_{\lambda i}$ for a layer of 10 microns depth is presented as a function of radiant exposure in ESH. The results for UV irradiance levels of 1 and 10 "Suns" are presented. It is seen that $\Delta\tau_{\lambda i}$ is larger at the 10 "Sun" irradiance for values of ESH > 200. For ESH < 200, $\Delta\tau_{\lambda i}$ is the same for both irradiance levels. The results shown in this figure, Fig. 12, in conjunction with those presented in Figs. 10 and 11, indicate that the time-irradiance reciprocity principle does not hold for materials with optical properties that change according to the photoreaction-diffusion model of solar degradation.

SECTION IX
CONCLUSIONS

A partial differential equation has been derived for the concentration of the ith defect specie generated in thermal control materials by a photoreaction-diffusion mechanism of solar degradation. This equation

has been solved to yield an analytical solution for the defect specie concentration, N_i. An analytical expression has also been obtained for the number $\dot{Q}_i$ of ith-type defects present in a layer of arbitrary depth and unit irradiated area. Thus, a theoretical model for solar degradation of thermal control materials can be formulated in mathematical terms and analytical solutions can be obtained for both the concentration and ·number of ith defects generated by solar UV radiation. These solutions may be used to calculate both the concentration and number of defects created in thermal control materials as a function of irradiation time and spectral irradiance. This is a significant step toward theoretically predicting the solar-induced optical absorptance change of spacecraft surfaces as a function of time since the induced absorptance change is ultimately a function of defect concentration.

The solutions for N_i and Q_i can also be used to better define the environmental parameters that must be controlled during solar radiation testing of thermal control coatings. For example, the equations for N_i and Q_i show that both the magnitude and spectral distribution of the solar simulator irradiance on the coating surface should be nearly equal to that of the sun in the wavelength interval $(0, \gamma_i)$. In addition, these equations indicate that the temperature of the irradiated material should be controlled during a solar radiation test and maintained at a value near that expected in flight. Also, the relations for N_i and Q_i show that solar radiation testing of thermal control coatings must be performed in a high vacuum, and measurement of radiative properties should be made in place. Finally, these solutions indicate that the time-irradiance reciprocity principle used in accelerated solar testing is invalid for materials which degrade according to the photoreaction-diffusion model.

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APPENDIX
ILLUSTRATIONS
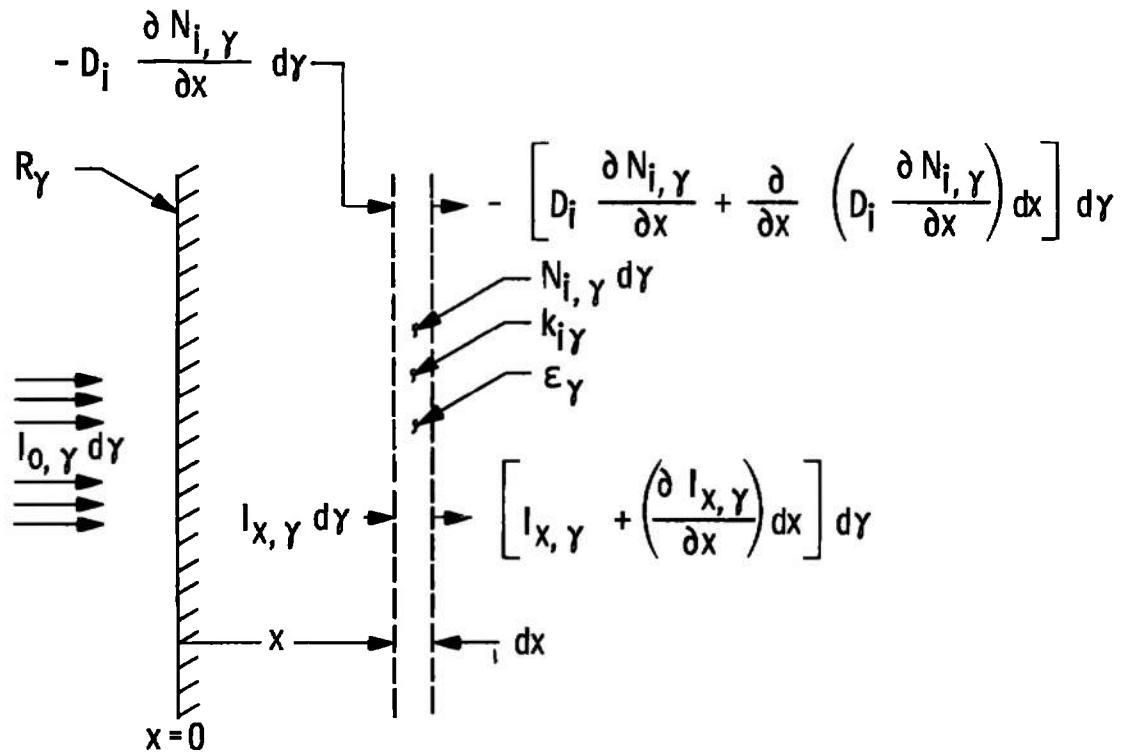
Fig. 1 Mathematical Model for Solar Degradation of Thermal Control Materials
by Photoreaction-Diffusion Damage Mechanism
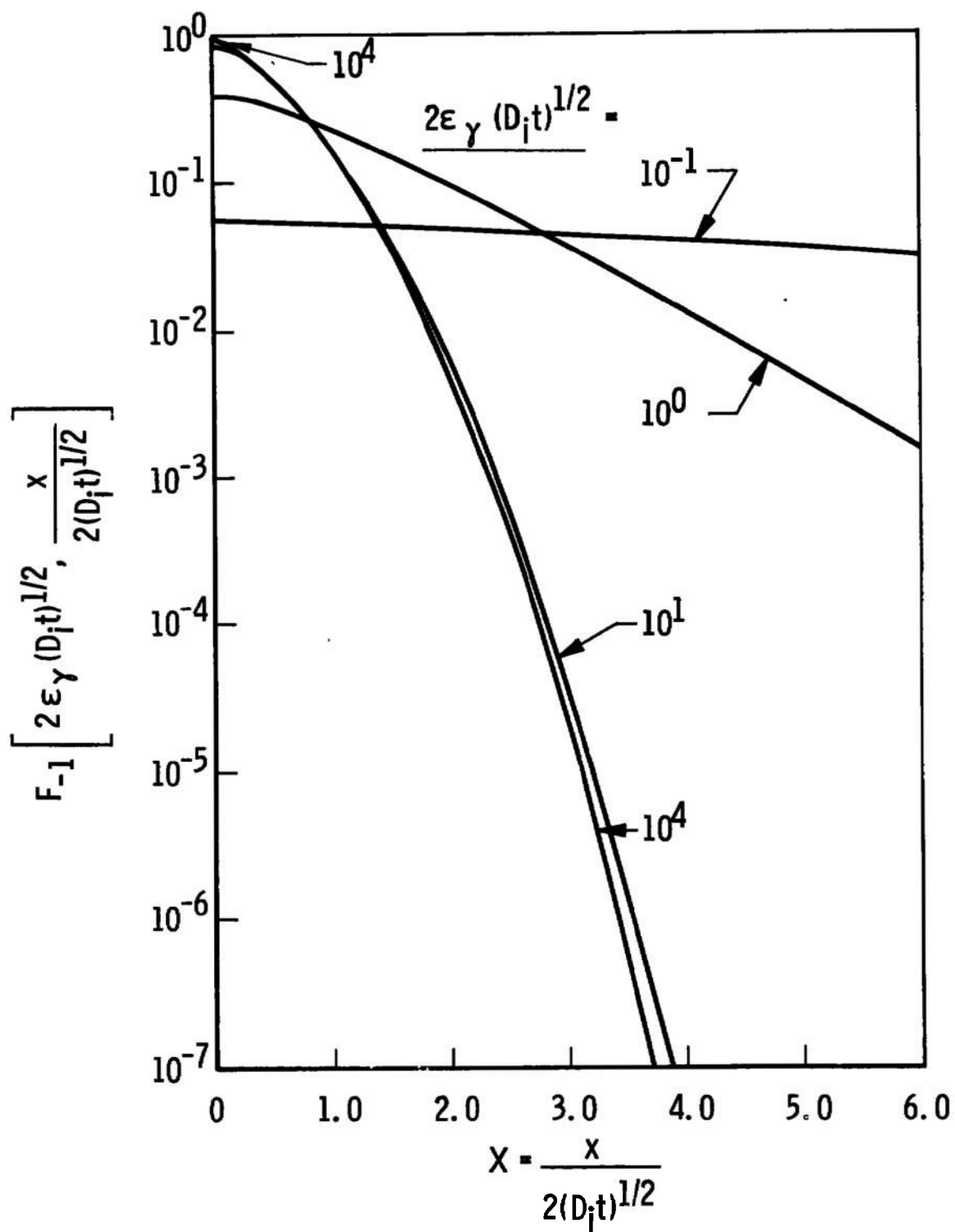
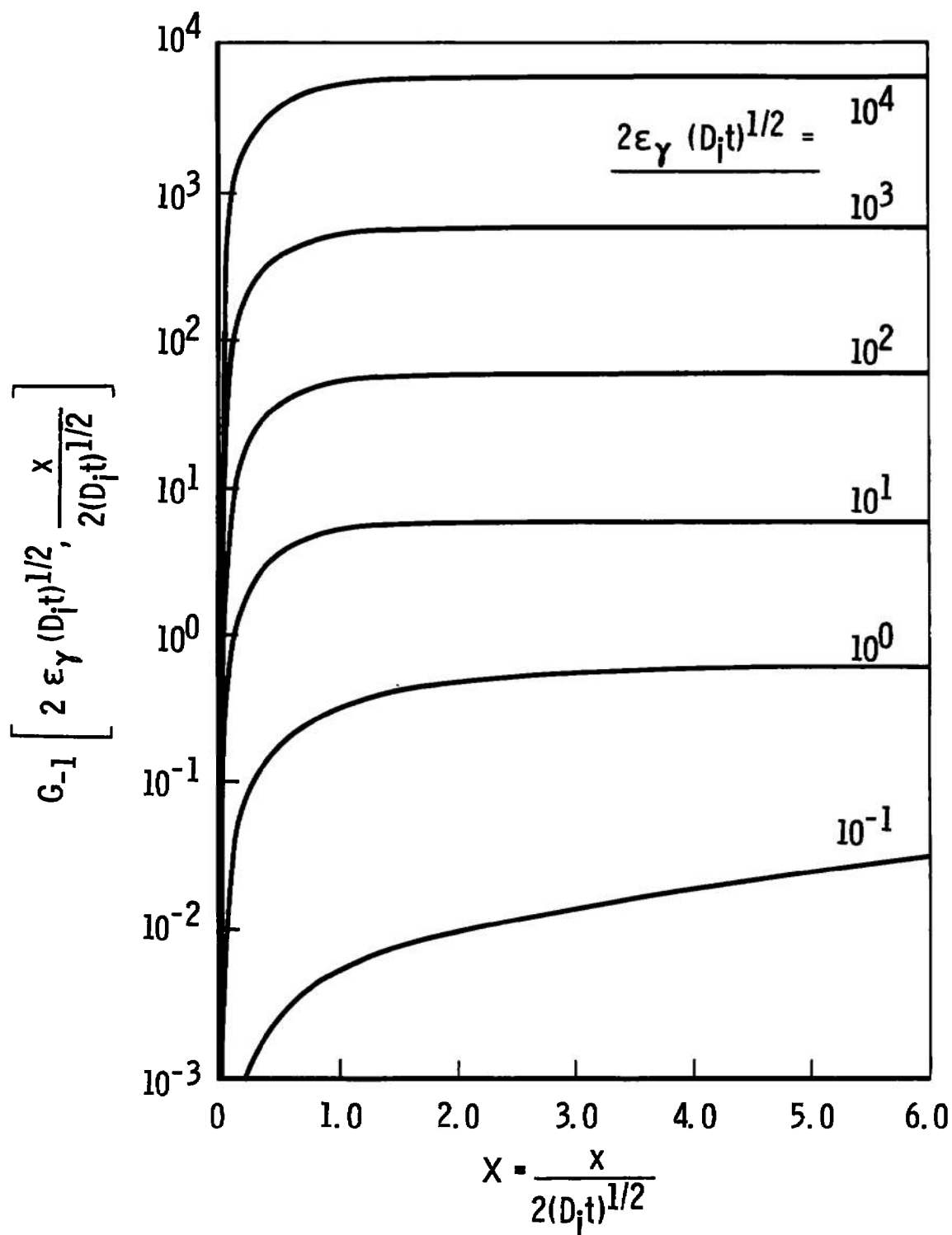Fig. 2 Dimensionless Function $F_{-1}\left[2\,\epsilon_\gamma(D_It)^{1/2},\ \frac{x}{2(D_It)^{1/2}}\right]$

Fig. 3 Dimensionless Function $G_{-1} \left[2 \epsilon \gamma \, (D_i t)^{1/2} \dfrac{x}{2(D_i t)^{1/2}} \right]$
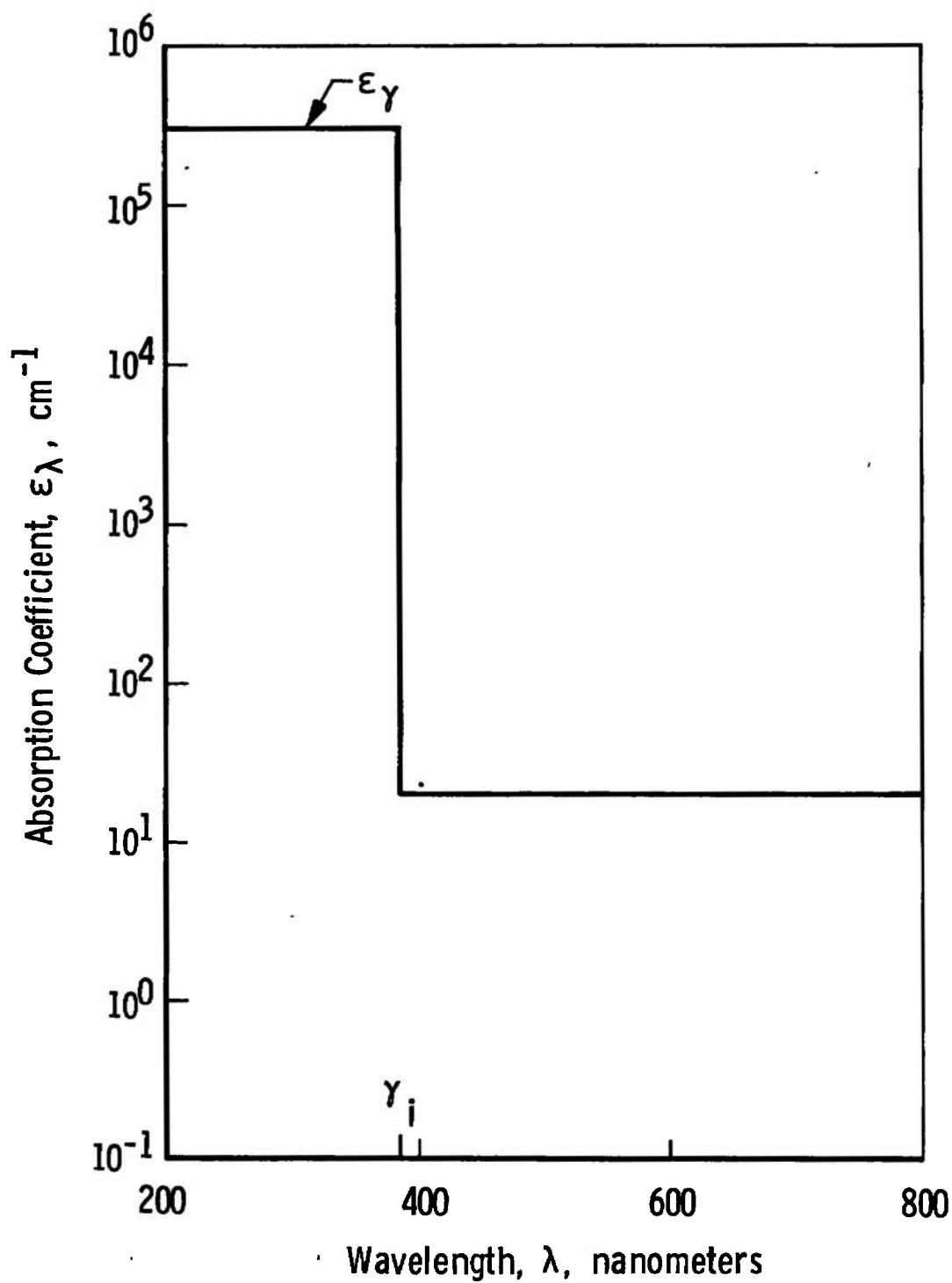
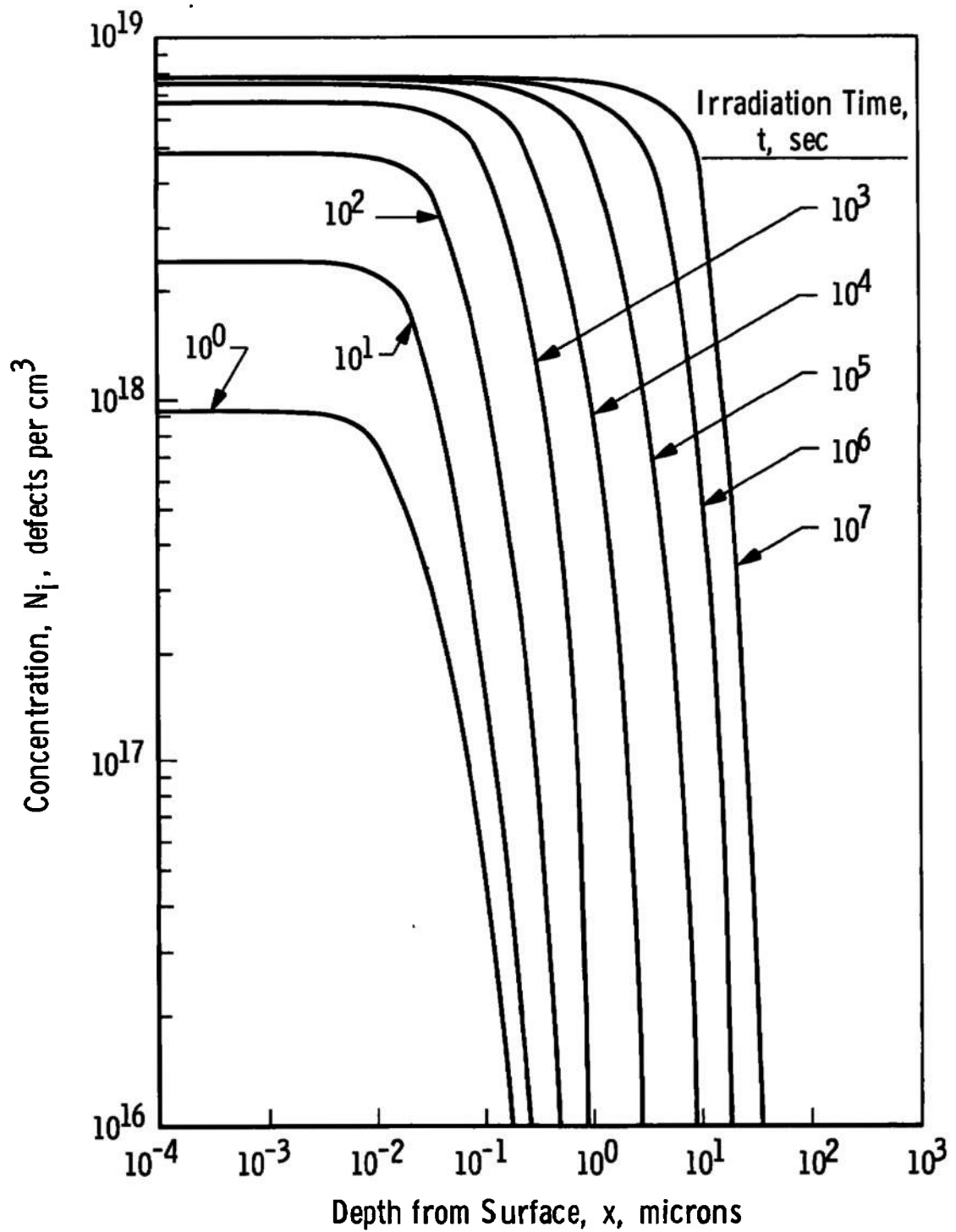Fig. 4 Spectral (Ultraviolet and Visible) Absorption Coefficient of Parent Material
prior to Irradiation

Fig. 5 Concentration Distribution of ith-Type Defects in Parent Material for an Ultraviolet Irradiance equal to that of the Sun
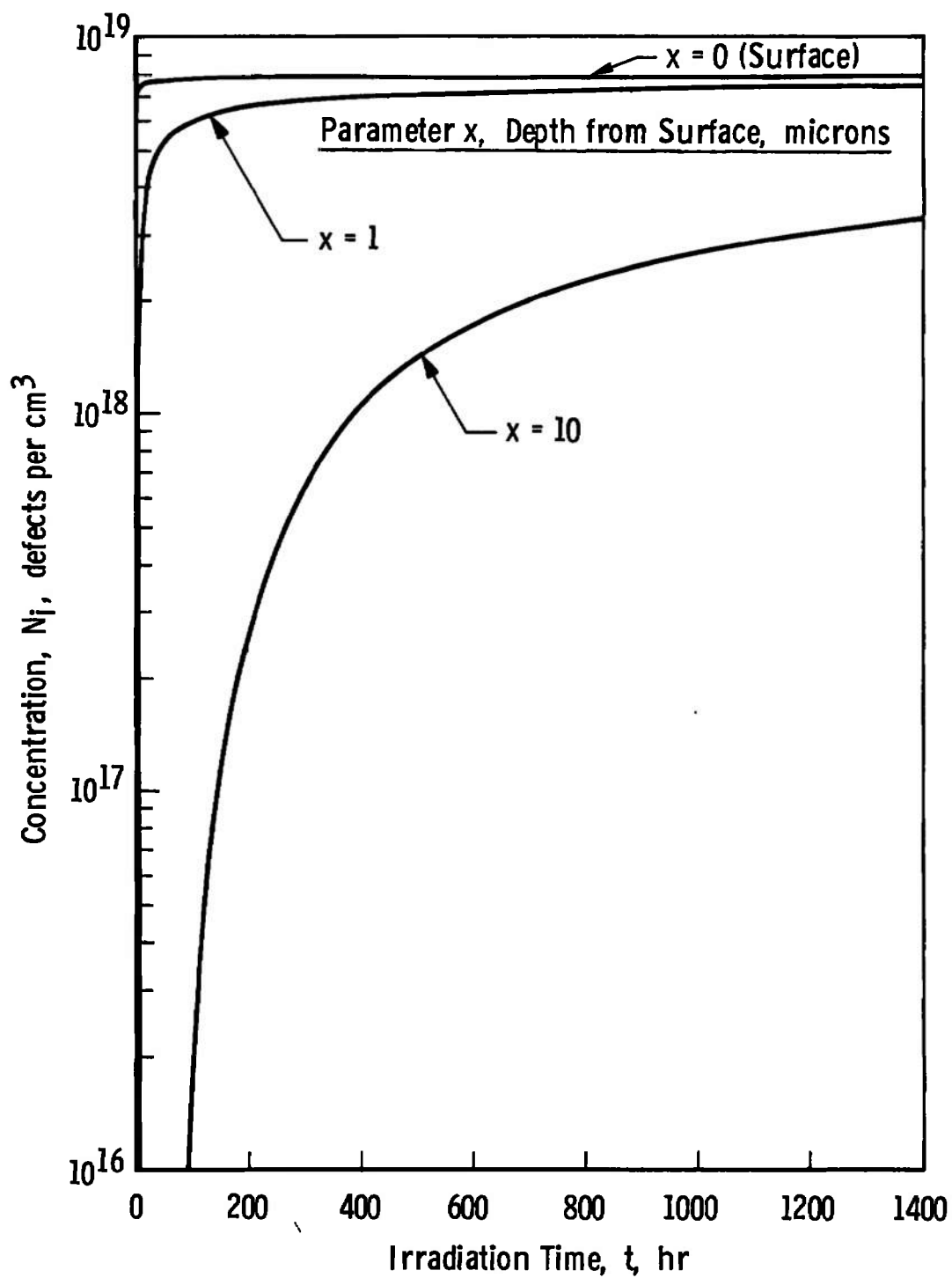
Fig. 6 Concentration of ith-Type Defects as a Function of Time Parent Material is Exposed to an Ultroviolet Irrodiance equal to thot of the Sun
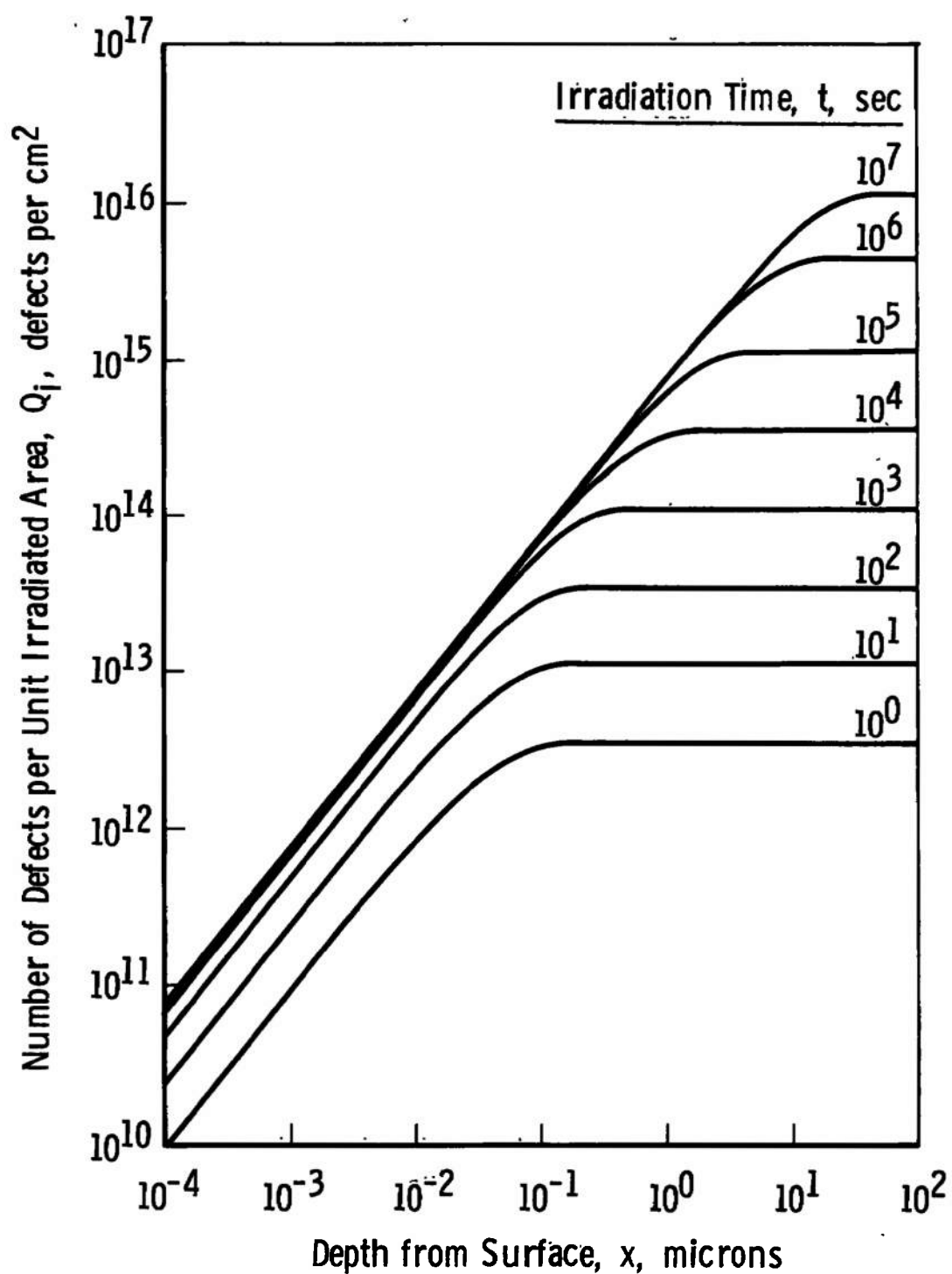
Fig. 7 Number of ith-Type Defects Present in Depth x of Parent Material for an Ultraviolet Irradiance equal to that of the Sun
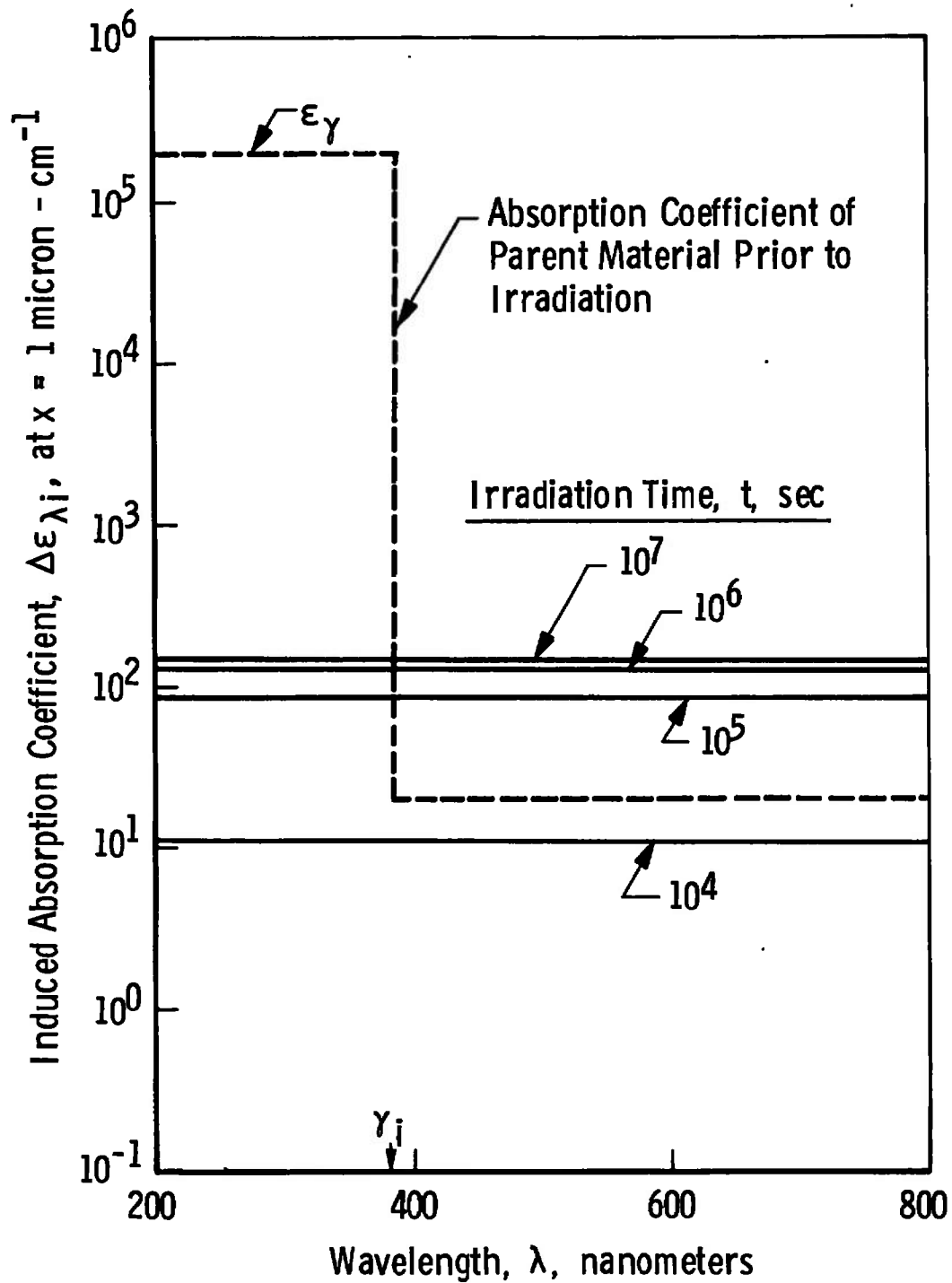
Fig. 8 Change in Parent Material Absorption Coefficient at x = 1.0 Micron
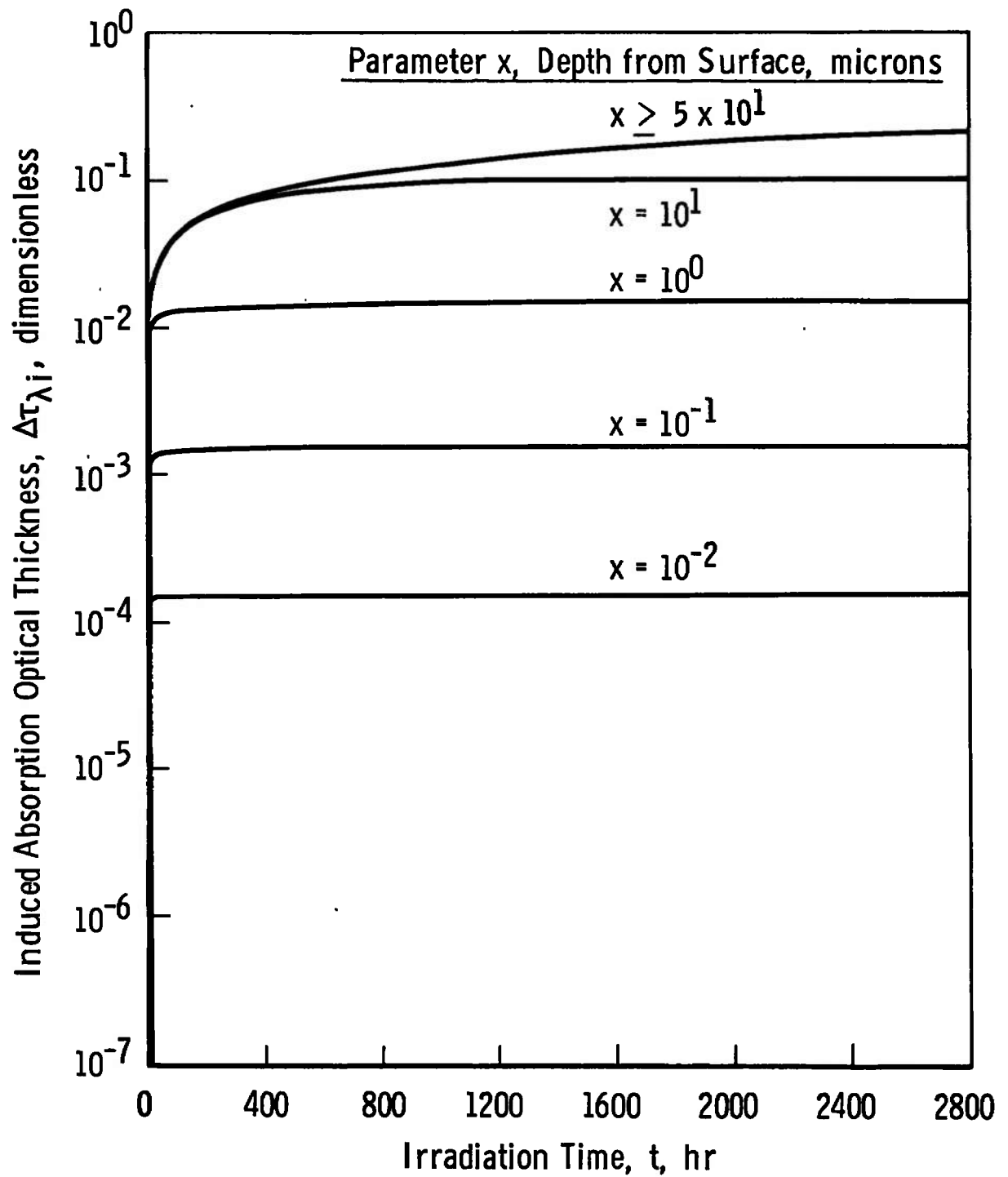for an Ultraviolet Irradiance equal to that of the Sun

Fig. 9 Change in Parent Material Absorption Optical Thickness for an Ultraviolet Irradiance Equal to that of the Sun
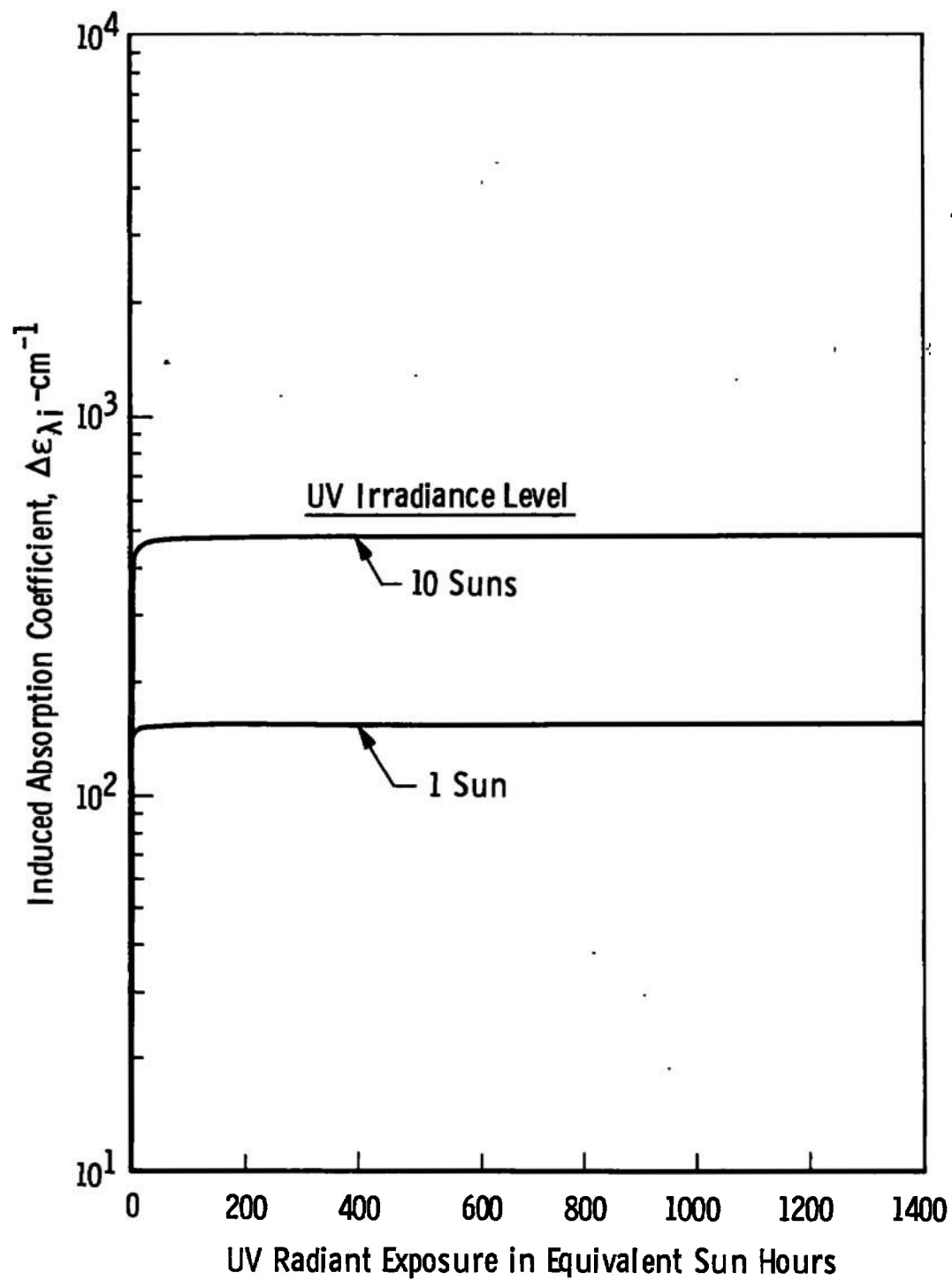
Fig. 10 Effect of Ultraviolet Irradiance Level on the Increase in Parent Material Absorption Coefficient at the Surface, $\Delta\epsilon_{\lambda i}(x = 0)$
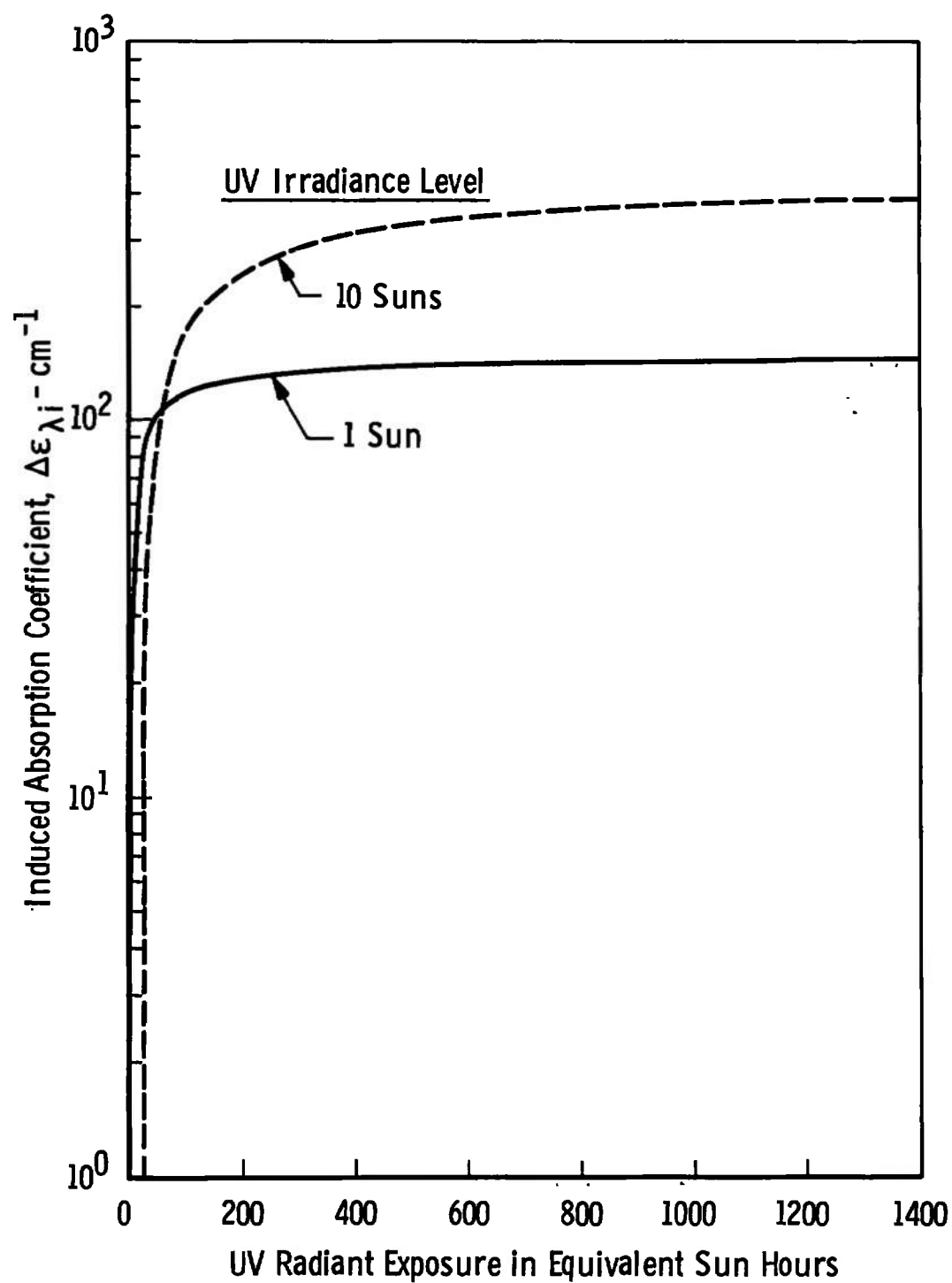
Fig. 11 Effect of Ultraviolet Irradiance Level on the Increase in Parent Material
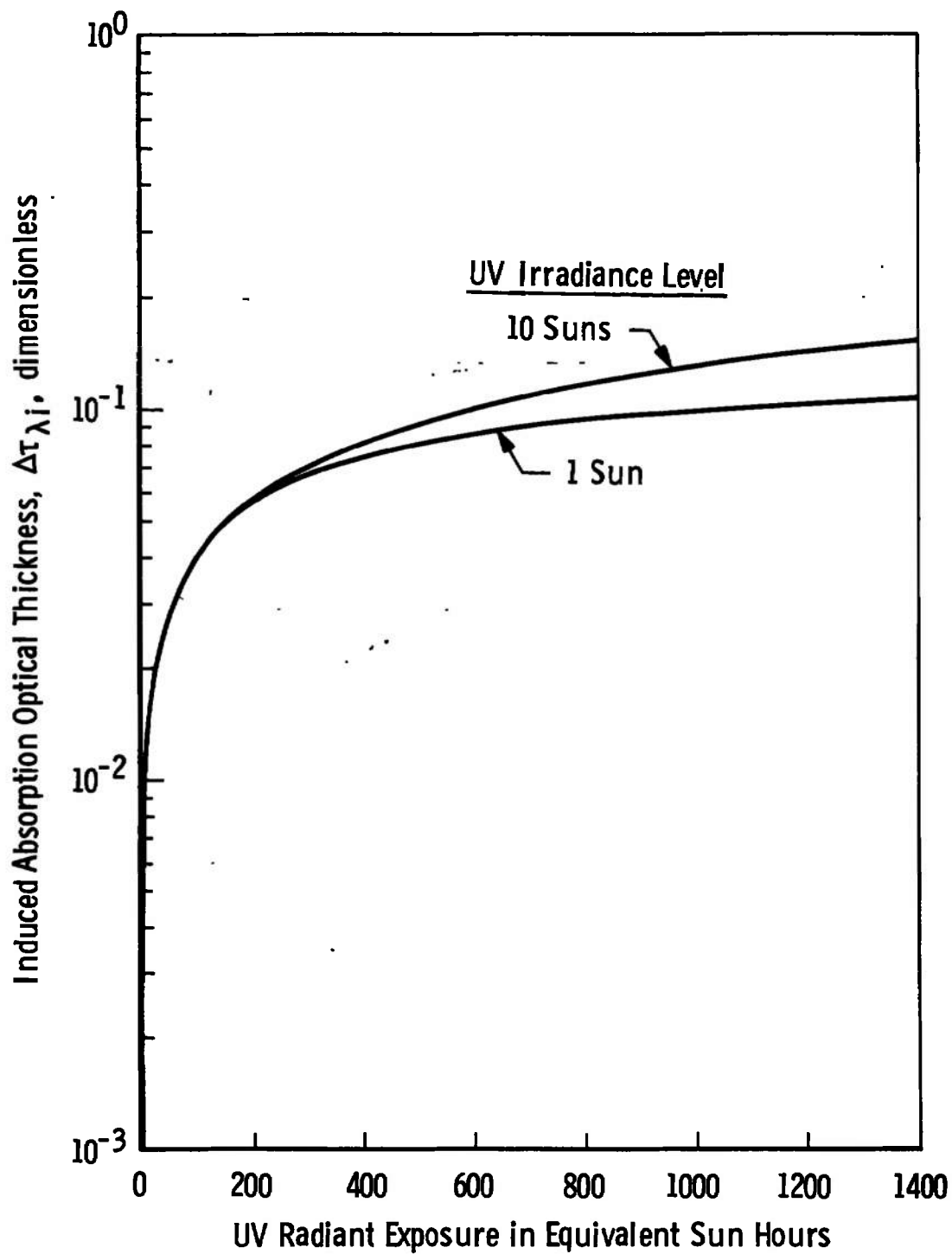Absorption Coefficient at a Depth of 1.0 Micron, $\Delta\epsilon_{\lambda i}$ (x = 1μ)

Fig. 12 Effect of Ultraviolet Irradiance Level on the Increase in Parent Material Aborption Optical Thickness at a Depth of 10 Microns, $\Delta\tau_{\lambda i}$ ($x = 10\mu$)

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13. ABSTRACT

A photoreaction-diffusion model for the solar degradation of thermal control materials is mathematically formulated and analyzed. The governing differential equation for the concentration of defect specie created in the material by radiation is derived, and an analytical solution is obtained for appropriate boundary conditions. From this solution for the concentration N_i of the ith-type defects, an analytical expression is derived for the number Q_i of ith-type defects present in a material layer of depth x and unit irradiated area. These analytical relations are used to predict the radiation-induced increase in the absorption coefficient and absorption optical thickness of a hypothetical thermal control material exposed to damaging ultraviolet irradiance equal to that of the sun. The solutions for N_i and Q_i are also used to better define the environmental parameters which must be controlled during solar radiation testing of thermal control coatings. For example, the time-irradiance reciprocity principle often employed in accelerated solar testing is investigated by use of the aforementioned solutions and is found to be invalid for materials which degrade according to the photoreaction-diffusion model.

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